Mechanism of hopping transport in disordered Mott insulators

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By using a combination of detailed experimental studies and simple theoretical arguments, we identify a novel mechanism characterizing the hopping transport in the Mott insulating phase of $Ca_{2-x}Sr_xRuO_4$ near the metal-insulator transition. The hopping exponent α shows a systematic evolution from a value of $\alpha = 1/2$ deeper in the insulator to the conventional Mott value $\alpha = 1/3$ closer to the transition. This behavior, which we argue to be a universal feature of disordered Mott systems close to the metal-insulator transition, is shown to reflect the gradual emergence of disorder-induced localized electronic states populating the Mott-Hubbard gap.

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The interplay of electron correlation and disorder near metal-insulator transitions represents one of the most fundamental, yet least understood problems in contemporary condensed matter physics. These issues are of particular importance in strongly correlated materials. For example, recent studies on manganites have revealed the emergence of coexisting clusters near the M-I transition, which plays a crucial role in the mechanism for colossal magnetoresistance [1]. Similar inhomogeneities have been observed in underdoped high-T_c cuprates, where spin glass and stripe formation feature disorder effects near the M-I transition [2]. Despite extensive experimental efforts [1, 2, 3], however, the effects of the intrinsic randomness on the doping/substitution in Mott transition systems remain largely an open problem, especially regarding the process of closing the Mott-Hubbard gap.

Among the Mott transition systems, the single layered ruthenate $Ca_{2-x}Sr_xRuO_4$ provides a rare case of the M-I transition that is highly susceptible to chemical pressure because of strong lattice-orbital coupling [4, 5, 6]. While one end member, Sr_2RuO_4 is a spin-triplet superconductor [7], complete substitution of isovalent Ca changes the superconductor into the Mott insulator Ca_2RuO_4 by introducing distortions to RuO_6 octahedra [8, 9, 10, 11]. The lattice deformation in both pure and Sr substituted Ca_2RuO_4 stabilizes the insulating state by inducing orbital polarization (orbital order) that creates a half-filled configuration near ε_F [12, 13, 14, 15, 16]. In addition, the results by both Raman and optical conductivity measurements indicate that the superexchange coupling J, and the effective bandwidth ($\propto \sqrt{J}$) in the insulating region are relatively insensitive to Sr content [13, 17]. Instead, the Sr substitution mainly controls the orbital polarization; the strong orbital polarization becomes gradually relaxed with substitution, but suddenly vanishes at the M-I transition to stabilize the metallic state [12, 13, 14, 15, 16].

This system is particularly suitable for the study of disorder effects in closing of the Mott-Hubbard gap because the isovalent Sr substitution provides statistical randomness without altering the key parameters: the net carrier density and the effective bandwidth. Furthermore, the variation in other parameters that usually complicates the analysis (crystal structure, phonon dispersions, etc.) should be small since a moderate substitution of Sr (< 10 %) is sufficient to suppress the Mott insulating state.

This paper presents the study of the effects of intrinsic randomness due to Sr substitution on the M-I transition in $Ca_{2-x}Sr_xRuO_4$. In this system, a well-defined Mott insulator appears at low Ts by the first order M-I transition in $0 \leq x < 0.2$. In the insulating phase, a systematic change in the transport and thermodynamic properties is observed, which elucidates the evolution of strongly localized states in closing the Mott-Hubbard gap. Furthermore, these localized states most likely reflect the tendency to spontaneously form inhomogeneities due to nano-scale phase separation in the vicinity of the Mott transition, as reported in other oxides [1, 2]. Our analysis reveals that this situation gives rise to a novel mechanism for hopping transport, unique to insulating phases of strongly correlated systems with moderate disorder.

Experiment. Single crystals of $Ca_{2-x}Sr_xRuO_4$ were prepared using a floating zone method [18]. The molten zone was well stirred during the growth to mix Ca/Sr homogeneously. X-ray powder diffraction show single phase samples without chemical segregation. Thus, Ca/Sr mixture provides a statistical disorder that prohibits classical percolation effects. Resistivity was measured by a standard four-probe dc technique. Magnetization was measured with a com1ercial SQUID magnetometer. Specific heat was measured by a thermal relaxation method.

Figure 1A presents the temperature dependence of the in-plane resistivity $\rho_{ab}(T)$ measured on cooling . While Ca_2RuO_4 ($x = 0$) is a Mott insulator at low T and exhibits a M-I transition above 300 K [8, 9, 10, 11], slight Sr substitution dramatically decreases the M-I transition temperature T_{M-I} to below 300 K. The transition is clearly seen by an abrupt increase of ρ_{ab} by a factor

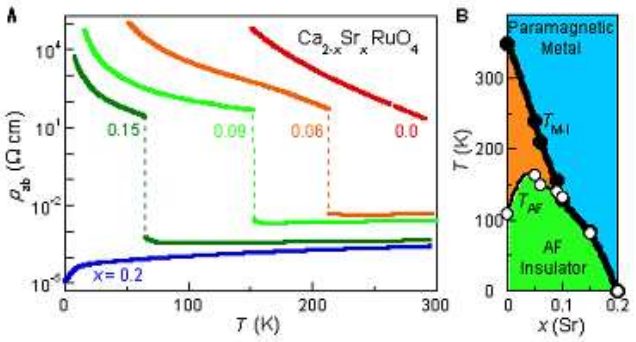

FIG. 1: (A) T dependence of the in-plane resistivity $\rho_{\rm ab}(T)$ measured on cooling for $Ca_{2-x}Sr_xRuO_4$. Vertical broken lines are guides to the eye. (B) Phase diagram for the region $0 \le x \le 0.2$ with three different phases: paramagnetic metal (blue), paramagnetic insulator (red), and antiferromagnetic insulator (green). $T_{\rm M-I}$ and $T_{\rm AF}$ are the M-I and AF transition temperatures determined on cooling. Thick and thin lines indicate the first and second order transitions.

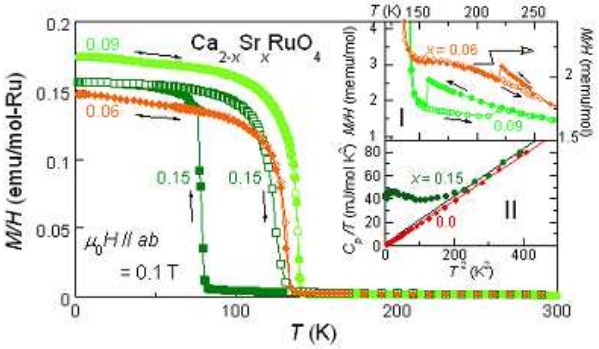

FIG. 2: T dependence of the in-plane susceptibility for $Ca_{2-x}Sr_xRuO_4$ with $x = 0.06$, 0.09, and 0.15. All curves were measured in a field-cooled sequence. The solid and open symbols indicate the results measured on cooling and heating, respectively. Inset: (I) thermal hystereses observed in the paramagnetic phase for $x = 0.06$ and 0.09. (II) C_P/T vs. T^2 for $x = 0$ and 0.15. The solid lines represent linear fit.

of more than 10^4. This change at $T_{\rm M-I}$ always involves large thermal hysteresis, indicating that the M-I transition is first order. This is due to the first-order structural transition that occurs simultaneously with the M-I transition [5]. Reflecting the quasi-two-dimensional electronic structure, the anisotropy $\rho_{\rm c}(T)/\rho_{\rm ab}(T)$ in the insulating phase reaches the value of the order of $10^3 - 10^4$ (not shown). As illustrated in Fig. 1A and 1B, $\rho_{\rm ab}$ in the metallic phase and $T_{\rm M-I}$, both rapidly decrease with x, and the system finally becomes fully metallic at $x = 0.2$.

In the insulating phase, an AF ordering appears as in Ca_2RuO_4. Figure 2 shows the T dependence of the in-plane component of the susceptibility $\chi(T)$ measured in a field-cooled sequence. The distinct increase in $\chi(T)$ at low T arises from canted AF, as clarified by neutron diffraction measurements [5]. The AF transitions are different in nature in the following two regions; in $0 \le x < 0.1$, the AF ordering occurs at $T < T_{\rm M-I}$ without any hystersis, while in $0.1 \le x \le 0.15$, it coincides with the M-I transition. In fact, as for $x = 0.06$ and 0.09, the M-I transition is reflected in the susceptibility hysteresis in the paramagnetic state (see the inset I of Fig. 2). The decrease of the paramagnetic χ at $T_{\rm M-I}$ is attributable to the disappearance of Pauli component in the insulating phase. However, at $x = 0.15$, a large hysteresis is observed at $T_{\rm AF}$, indicating that both M-I and AF transitions at $x = 0.15$ occurs concomitantly with the first order structural transition.

Here, we note two important facts that confirm the Mott insulating ground state in $0 \le x < 0.2$. First, the AF ordering occurs only in the insulating phase. Second, $\rho(T)$ does not show any anomaly at $T_{\rm AF}$ for $x = 0.06$ and 0.09. These facts agree well with the significant feature of Mott insulators: the separation between charge and spin degrees of freedom due to a large charge (Mott-Hubbard) gap compared to low energy spin excitations.

Observation of hopping transport. In order to elucidate the electronic state in the insulating phase, we analyze $\rho_{\rm ab}(T)$ shown in Fig. 1A. The result of Ca_2RuO_4 ($x = 0$) fits well to activation type insulating behavior

$$\rho_{\rm ab}(T) = A\exp(E_{\rm G}/2k_{\rm B}T) \qquad (1)$$

below 250 K to the lowest T measured, giving $E_{\rm G} \simeq$ 4500 K, consistent with the gap observed by the optical conductivity measurements [14, 19]. Since Ca_2RuO_4 is a Mott insulator, $E_{\rm G}$ should give the gap size between the upper and lower Hubbard bands (UHB and LHB).

Variable-range hopping (VRH) conduction

$$\rho_{\rm ab}(T) = A\exp(T_0/T)^{\alpha} \qquad (2)$$

with $\alpha = 1/2$ also describes the T dependence over almost the same T region in agreement with Ref. [10]. VRH is usually observed in systems with strongly localized states near $\varepsilon_{\rm F}$. However, fitting of the resistivity in a limited region alone does not give conclusive evidence for the presence of localized electronic states. In the case of Ca_2RuO_4, we measured the specific heat $C_P(T)$ and found the electronic specific heat coefficient γ to be 0 ± 0.5 mJ/molK^2, as shown in the inset II of Fig. 2. Therefore, it is most likely that there are no localized states near $\varepsilon_{\rm F}$ and that activation-type behavior is the consistent interpretation of the low T transport in Ca_2RuO_4.

To obtain the systematic estimate of $E_{\rm G}$, we also try to fit the $\rho(T)$ curve for each x to Eq. (1). However, the well fitted region becomes rapidly narrower with x, indicating that the Sr substituted region does not obey activated behavior. In contrast, as in Fig. 3A, the VRH widely describes the insulating behavior. Equation (2)

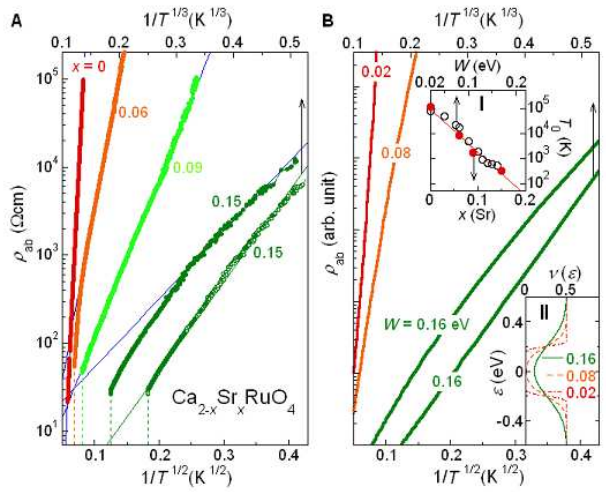

FIG. 3: (A) $\ln\rho$ vs. $1/T^{1/2}$ and $1/T^{1/3}$ for the insulating phase of $Ca_{2-x}Sr_xRuO_4$. The results for $x \leq 0.09$ are plotted against the lower horizontal axis $1/T^{1/2}$, while these for $x = 0.15$ are plotted against both $1/T^{1/2}$ and the upper axis $1/T^{1/3}$. Straight lines indicate a fitting result to Eq. (2). (B) Corresponding plot for theoretical predictions. The results for $W = 0.02$ and 0.08 eV are plotted against the lower axis $1/T^{1/2}$, while these for $W = 0.16$ eV are plotted against both $1/T^{1/2}$ and the upper axis $1/T^{1/3}$. Inset: (I) T_0 obtained by fitting of $\rho(T)$ to Eq. (2) with $\alpha = 1/2$ for $Ca_{2-x}Sr_xRuO_4$ (solid circle) as a function of x (lower axis), and for theory (open circle) as a function of W (upper axis). (II) Model band structure used in our calculation. As the disorder increases (W : 0.02 eV $\rightarrow$ 0.16 eV), the band-tails gradually fill-in the Mott gap, producing a soft gap similar to that predicted by Efros and Shklovskii, but on a much larger energy scale.

with $\alpha = 1/2$ describes $\rho_{ab}(T)$ for $x = 0.06$ and 0.09 over a respectable temperature range: 236 K-150 K ($x = 0$), 155 K-46 K (0.06), 152 K-14.0 K (0.09), and 21 K-7.3 K (0.15). It should be noted that $\rho_{ab}(T)$ obeys VRH with $\alpha = 1/2$ over a decade of T for $x = 0.09$ and over a comparable range for $x = 0.06$. The x dependence of the fitting parameter T_0 is given in the inset I of Fig. 3B, showing exponential decrease with x.

For the highest Sr concentration $x = 0.15$, $\rho_{ab}(T)$ does not follow Eq. (2) well with $\alpha = 1/2$, but better fits are obtained with a smaller value of the exponent $\alpha = 1/3$ over a decade of T (5 K - 65 K), as shown in Fig. 3A. The fit gives $T_0 = 8.8 \times 10^3$ K. This value of the hopping exponent α is consistent with two-dimensional (2D) transport, within the Mott VRH picture [20]. Because our system has essentially a quasi 2D electronic structure with large anisotropy $\rho_c/\rho_{ab} \approx 10^3$ in the insulating phase, 2D hopping seems a natural choice.

Origin of hopping transport. Generally, in the process of carrier doping in conventional semiconductors such as Si and Ge, the evolution of the transport behavior from simple activation to Efros-Shklovskii (ES) VRH (Eq. (2) with $\alpha = 1/2$) and finally to Mott VRH has been observed, as the localized states fill in the band gap [21]. The Mott VRH, observed at $x = 0.15$ for a decade of T, usually appears when the system has a localized band with a nearly constant density of states (DOS) $\nu(\varepsilon)$ around ε_F. The low temperature C_P/T for $x = 0.15$ is well described by $\gamma + \beta T^2$ with the same Debye temperature $\Theta_D = 410$ K as Ca_2RuO_4 (411 K) and Sr_2RuO_4 (410 K) (Inset II of Fig. 2). The electronic contribution γ is about 1.5 ± 0.5 mJ/molK^2. The extra entropy release of 0.36 J/mol K due to the increase in C_P/T below 14 K is much smaller than $R\ln 3 = 9.13$ J/mol K expected for $S = 1$ moment at each Ru site, and is attributable to the freezing of the uncorrelated spins induced by disorder. Therefore, the γ value above should give an appropriate estimate of $\nu(\varepsilon_F)$ at $T > 14$ K. For 2D Mott VRH, the localization length ξ can be estimated using the formula $k_B T_0 \simeq 8.6/\nu(\varepsilon_F)\xi^2 d$, where d is interlayer spacing. Our results yield a reasonable value of $\xi \approx 25$ Å, that is several times the Ru-Ru interatomic spacing (≈ 3.8 Å).

In contrast, Efros-Shklovskii VRH usually appears when the long-range Coulomb interaction between localized electrons is important, forming the so-called Coulomb gap (CG) with $\nu(\varepsilon) \propto |\varepsilon - \varepsilon_F|$ in 2D [21]. This leads to VRH with $\alpha = 1/2$ and $k_B T_0 \simeq e^2/\kappa\xi$, where κ is a dielectric constant. However, T_0 observed in our system (Inset I of Fig. 3B) is too large for long range Coulomb interaction. In fact, assuming $\kappa \approx 100$ as in Ca_2RuO_4 [10], we obtain ξ of the order of 0.03 Åfor $x = 0.06$, which is not physically meaningful. Correspondingly, the energy scale of fitting regions ($T \leq 150$ K) is also much too high in comparison with the ordinary size of CG (10-100 K) for semiconductors [21]. It is therefore unlikely that the emergence of the Coulomb gap is the physical origin of the apparent ES-like behavior.

What could then lie at the origin of the observed VRH with $\alpha \approx 1/2$? To answer this question, we note that the gap-type structure in the DOS is essential for the exponent $\alpha = 1/2$; The standard Mott VRH picture assumes an energy-independent DOS, leading to a small hopping exponent $\alpha = 1/3$ in 2D, while the formation of the CG gives a strongly energy-dependent DOS, which in turn produces a larger hopping exponent $\alpha = 1/2$. However, we have seen that the CG is too small to account for our observations. Instead, given the large energy scale of both the fitting region and T_0, the energy gap has to be $0.1 - 1$ eV, which actually fits well in the range of the Mott gap. Since the insulating phase of our system is a Mott insulator, we propose that the disorder-modified Mott gap lies at the origin of the VRH with $\alpha \approx 1/2$, as a new mechanism distinct from the ES scenario.

Materials near a first-order transition separating two competing ground states are generally fragile against phase separation; moderate randomness can create coexisting clusters of competing ordered states [1]. In our case, the first order M-I transition separates the Mott

insulating phase and the paramagnetic metallic phase. The statistical distribution of Ca/Sr inevitably creates (although small) the locally Sr-rich region with a broader *local* bandwidth. This statistical distribution of the local bandwidth should create extended tails of both UHB and LHB at their edges, which are easily localized. As the system approaches the metallic phase, the band tails extend deeper into the Fermi level region by enhancing their DOS. Finally, for large enough x(Sr), these tails are expected to overlap and produce strongly localized states near $\varepsilon_{\rm F}$. As the intrinsic disorder steadily increases, we thus expect the behavior to gradually cross over from activated, to ES-like VRH, and finally to Mott-like VRH. This is exactly what is observed in our experiment.

Theory. To put these physical ideas on a more rigorous basis, we now present a simple theoretical model for hopping transport in disordered Mott insulators. First, we generalize the arguments of Mott [20] and Efros-Shklovskii [21] to a situation where the DOS has an arbitrary energy dependence. According to these approaches, the transition probability between two localized states is

$$\sigma = \sigma_o \exp\{-2R/\xi - \varepsilon_o(R)/k_{\rm B}T\}, \qquad (3)$$

where σ_o is an "attempt frequency," R is the distance between the two sites, $\varepsilon_o(R)$ is their energy difference, and ξ is the localization length. The further the sites are from each other, the smaller the wave-function overlap between the two states. However, sites with small energy difference are typically more distant from each other. The lowest energy $\varepsilon_o(R)$ of the accessible state within a radius R from a given site is implicitly given (in 2D) by the solution of

$$1 = \pi R^2 H(\varepsilon_o(R)), \qquad (4)$$

where $H(\varepsilon) = \int_o^{\varepsilon} \nu(\varepsilon')d\varepsilon'$. At any given temperature, the most probable hopping distance R is determined by minimizing the exponent of Eq. (3), giving

$$\frac{1}{\xi} = \frac{(\pi H(\varepsilon_o))^{3/2}}{\pi\nu(\varepsilon_o)k_{\rm B}T}. \qquad (5)$$

The solution of these equations determines $R(T)$ and thus $\varepsilon_o(T)$, which should be substituted in Eq. (3), to obtain the desired T-dependent resistivity $\rho(T) \sim 1/\sigma$. For the special cases of constant or linear forms for $\nu(\varepsilon)$, these equations can be solved analytically, reproducing the respective Mott ($\alpha = 1/3$) or Efros-Shklovskii ($\alpha = 1/2$) hopping laws. In our case, $\nu(\varepsilon)$ assumes a more complex form, and a numerical solution is necessary. Given our fortuitous situation where the Sr substitution does not make significant change in net carrier density nor effective bandwidth, we chose a simple model for $\nu(\varepsilon)$. Specifically, we take the UHB and LHB to have constant DOS and bandwidth of 1 eV, with a gap of 0.4 eV, and $\xi = 28$ Å, which corresponds to our material. The effect of disorder is described by introducing gaussian band-tails of width W, which tend to gradually fill-in the gap, as shown in the inset II of Fig. 3B. We examine the evolution of $\rho(T)$ and the fitting parameter T_0 to VRH with the exponent $\alpha = 1/2$, as a function of disorder W. The theoretical results are presented in Fig. 3B for $\rho(T)$ in the same fashion as the experimental ones in Fig. 3A, and in the inset I of Fig. 3B for $T_0(W)$. The theory is able to reproduce all the qualitative and even some quantitative aspect of the experimental data for both $\rho(T)$ and T_0, giving strong support to the proposed physical picture.

In summary, detailed analysis of the Mott insulating phase in $Ca_{2-x}Sr_xRuO_4$ reveals that the Sr substitution to Ca_2RuO_4 changes transport from the activation type to the variable-range-hopping. The moderate randomness intrinsic to the Sr substitution leads to the formation of strongly localized states around the closing of the Mott-Hubbard gap. As a result, hopping transport emerges of the form similar to that predicted by Efros and Shklovskii, but with a distinctly different physical origin, and on a distinctly different energy scale.

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